

USE OF ELECTROPLATING SLUDGE FOR CERAMIC BRICK MANUFACTURE

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The migration of heavy metal ions (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cr^{6+} , Ni^{2+} , Fe^{2+} and Fe^{3+}) from ceramic brick containing sludge from electroplating is investigated. The laws of migration of chemical elements under the action of different factors (temperature and time of exposure, pH of model medium) in relation to the batch and chemical composition of the bodies as well as the structure and phase composition of the materials are established. The optimal content of sludge in the bodies for obtaining ceramic brick, completely satisfying the regulatory requirements regarding the migration of chemical elements, is determined.

Key words: ceramic brick, sludge from electroplating, heavy metals, migration, model medium, photometry, atomic absorption spectroscopy, structure, maximum admissible concentration.

The demand for high-quality, durable construction materials, including, once again, facing and masonry brick with the required decorative and physical-technical characteristics, continues to increase together with the construction volumes, including the construction of individual homes. Because of the low quality of the polymineral low-melting clayey raw material from Belarus used to obtain brick different additives must introduced into the ceramic bodies. On the basis of the published data [1] and research [2] we chose as the fluxing-inert component of the body iron-containing wastes from electroplating, which make it possible to adjust the technological properties of ceramic bodies and the color and physical-technical characteristics of the finished articles as well as to solve the problems of conservation of resources, recycling industrial wastes and environmental protection.

The study of ceramic bodies based on polymineral low-melting clay from the Zapol'e deposit and sludge from electroplating work done at the leading enterprises in Belarus [S. M. Kirov Gomel' Machine Tool Plant (Republic of Belarus), Raton JSC (Gomel'), Minsk Tractor Plant, Gomel' Casting and Normals Plant, Atlant JSC and Belorussian Metallurgical Plant] showed that iron-containing wastes can be used in principle to obtain facing and ordinary ceramic brick and stone. The materials obtained using bodies with optimal composition, including 15–25%³ sludge and 75–85% clay from the Zapol'e deposit, are characterized by saturated red, red-brown and chocolate colors and the required physi-

cal-technical properties: water absorption 13.8–20.9%, compression strength 25.1–33.9 MPa and freeze resistance ≥ 50 cycles of alternating freezing and thawing [2].

At the same time the problem of adverse effects due to heavy metals on the environment during reprocessing of wastes and due to the finished materials obtained from them remains urgent. It is known that the brickwork of buildings is periodically exposed to acidic atmospheric precipitation, mechanical damage and other factors resulting in structural degradation and enabling heavy-metal ions to migrate out of the building material. Possessing high biological and migration activity they penetrate into plants and create an indirect hazard to humans. This makes it necessary to monitor the level of migration of heavy-metal ions from ceramic brick obtained using electroplating sludge.

The few available studies of the migration of chemical elements from ceramic materials mainly concern glassy coatings and glazed and enameled articles in contact with food products [3, 4]. In addition, today, in the Republic of Belarus there is still no unified method of determining the environmental safety of building materials made using industry wastes.

In this connection, the aim of the present work was to study the laws of migration of chemical elements from ceramic brick under the action of different factors (temperature and exposure time, pH of the model medium) in relation to the batch and chemical composition of the bodies as well as the structure and phase composition of the material.

Samples of ceramic brick obtained on the basis of clay from the Zapol'e deposit and sludge from the Gomel' Casting and Normals Plant (GCP) by semidry pressing followed

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³ Here and below, content by weight, wt.%.

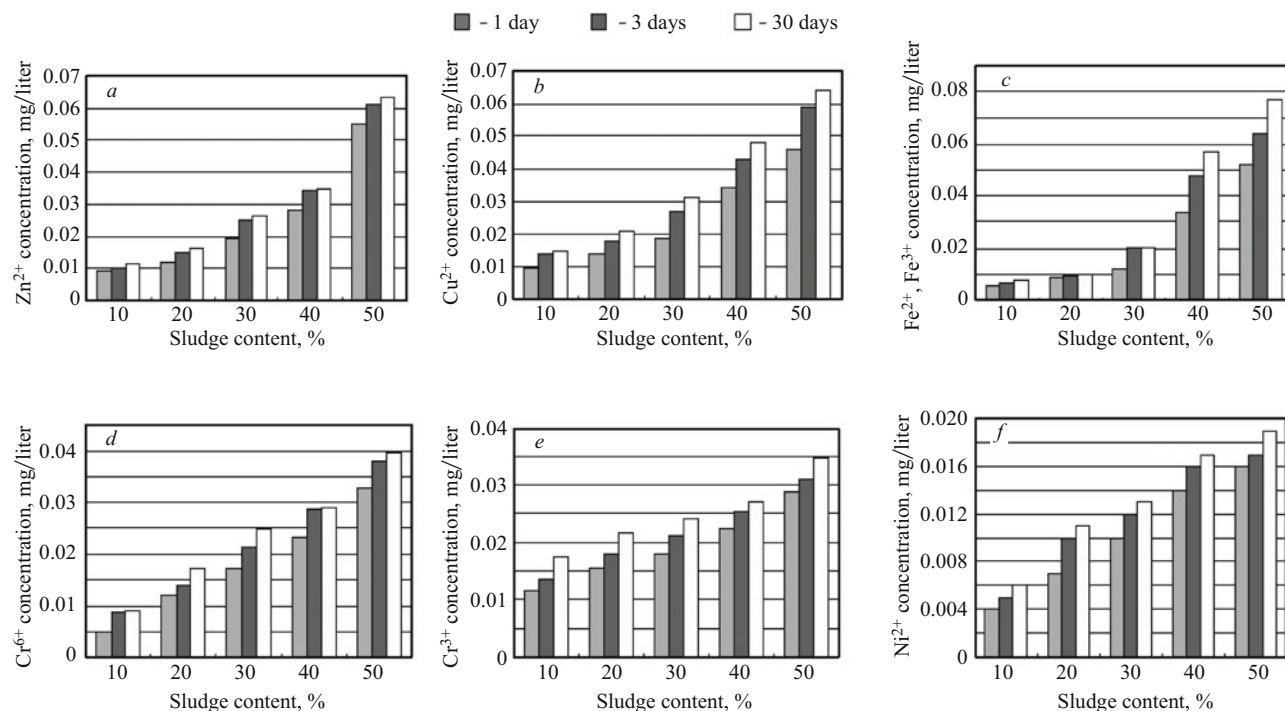


Fig. 1. Migration of chemical elements from ceramic brick samples into distilled water (exposure temperature 20°C).

by kilning at $1050 \pm 10^\circ\text{C}$ were studied. The instructions in [7] concerning the sanitary-hygienic assessment of building materials made with the addition of industrial wastes were used to study migration. The solutions (extracts) used to determine the degree of migration of chemical elements were prepared by isothermal soaking at temperatures 20 ± 2 , 35 ± 2 and $50 \pm 2^\circ\text{C}$ of the experimental samples in the form of cylinders 30 ± 1 mm in diameter and 15 ± 1 mm high in a model medium comprising distilled water or ammonium-acetate buffer solution characterized by pH 4.5. The exposure times were 1, 3 and 30 days. Since ceramic brick periodically comes into contact briefly with atmospheric precipitation, the sample – medium volume ratio was 1 : 10. To approximate the real conditions as closely as possible samples with cleavage surfaces comprising about 7 – 10% were studied; this made it possible to simulate some breakdown of the material in use.

Analysis of the chemical composition of the GCP sludge and ceramic bodies based on this sludge made it possible to single out a list of chemical elements whose concentration must be controlled in the water extracts. The ions Zn^{2+} , Cu^{2+} , Cr^{3+} , Cr^{6+} , Ni^{2+} , Fe^{2+} and Fe^{3+} present the greatest hazard.

The concentrations of Zn^{2+} and Cu^{2+} present together in the extracts obtained were determined by anodic inversion voltammetry with an AVA-1 voltammetric analyzer coupled with a computer, while the Cr^{3+} , Cr^{6+} , Ni^{2+} , Fe^{2+} and Fe^{3+} concentrations were determined by the photometric method with a KFK-3-01 ZOMZ photoelectric colorimeter. The procedures followed in the analysis are described in detail in [6].

In addition, atomic absorption analysis with an Avanta GM spectrometer (Germany) was used to study the concentrations of the chemical elements. The values obtained for the concentrations of the ions studied were compared with the maximum admissible concentrations of these elements in the fresh water and residential water supply systems, presented in GN 2.1.5.10-21–2003 [7].

According to the diagrams in Fig. 1, at 20°C increasing the exposure time in distilled water from 1 to 30 days and simultaneously increasing the content of GCP sludge in the samples from 10 to 50% increases the zinc and copper ion concentrations from 0.009 to 0.063 and 0.0094 – 0.0640 mg/liter, respectively, which does not exceed the MAC, equal to 1 mg/liter. The total concentration of the ions Fe^{3+} and Fe^{2+} in the experimental samples is 0.052 – 0.077 mg/liter, which is much lower than the MAC, equal to 0.3 mg/liter. The Cr^{6+} and Cr^{3+} concentrations in the experimental extracts are, respectively, 0.005 – 0.04 and 0.036 – 0.347 mg/liter, while the MACs for hexa- and trivalent chromium are 0.05 and 0.5 mg/liter, respectively. The nickel ion content is 0.004 – 0.01 mg/liter, which completely satisfies the regulatory requirements.

Analysis of the data shows that increasing the sludge content in the bodies from 10 to 50% and the exposure time of the samples from 1 to 30 days increases the concentration of the experimental ions in the water extracts, 60 – 80% of the ions of each experimental element migrating on the first day.

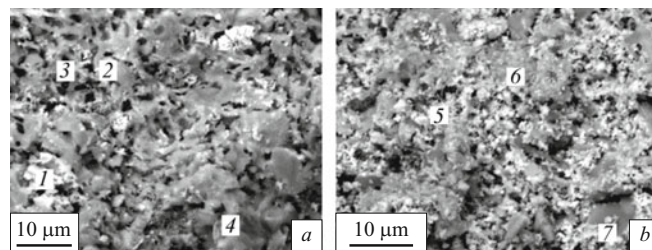
TABLE 1. Concentration of Heavy Metal Ions in Extracts and Their Migration from Ceramic Brick Samples

GCP sludge content, wt. %	Ions	Ion concentration, mg/liter			Migration, %
		according to photometry	AAS method	maximum possible	
10	Ni ²⁺	0.009	0.00	66.00	0.014
30		0.016	0.01	198.00	0.0085
50		0.025	0.02	330.00	0.0075
10	Fe ²⁺ , Fe ³⁺	0.040	0.05	9791.86	0.0003
30		0.130	0.18	29375.59	0.0004
50		0.410	0.44	48959.31	0.0006
10	Cr ³⁺ , Cr ⁶⁺	0.251	0.22	874.36	0.030
30		0.415	0.35	2623.08	0.015
50		0.643	0.61	4371.80	0.010
10	Cu ²⁺	0.123	0.16	19.17	0.640
30		0.189	0.21	57.52	0.330
50		0.462	0.50	95.86	0.490
10	Zn ²⁺	0.137	0.09	388.90	0.033
30		0.324	0.28	1166.71	0.027
50		0.550	0.56	1944.55	0.028

It is known that even if no pollutants are present in air, atmospheric precipitation is acidic (pH \approx 5.6) due to carbon dioxide gas present in the air being dissolved and carbonic acid H₂CO₃ formed. In the modern industrial world the elevated amount of sulfur and nitrogen oxides in the atmosphere creates excess acidity in rain (pH < 5.0). In this connection, the action of an acidic model medium characterized by pH = 4.5 on the degree of migration of heavy-metal ions at holding temperature 20°C for 30 days was studied.

Analysis of the results shows that the migration of all the experimental elements increases at moderate exposure. Thus, the concentration of Ni²⁺, Cr⁶⁺ and Cr³⁺ increases 1.31 – 1.85-fold, Fe²⁺ and Fe³⁺ 3.5-fold and zinc and copper ions 9.1 – 10.2- and 5.9 – 8.2-fold, respectively. In addition, the concentration of copper, zinc and nickel in ammonium-acetate extracts obtained from samples with the maximum content of GCP sludge is much lower than the maximum admissible. The total content of iron ions is at the MAC level and equals 0.294 mg/liter. In the case of the extracts obtained by exposure of samples containing 50% sludge maximum levels permitted by the regulations are exceeded by very small amounts 0.0803 and 0.0097 mg/liter for tri- and hexavalent chromium, respectively.

Since during the summer sunlight can heat a masonry surface by up to 40 – 50°C, the effect of temperature on the migration of heavy-metal ions from ceramic brick samples was also studied. To create more stringent operating conditions for the ceramic articles as close as possible to the real conditions, the samples were kept for 30 days in a model medium, consisting of an ammonium-acetate buffer solution with pH = 4.5 at the temperatures 20, 35 and 50°C. The re-

**Fig. 2.** Electron microscope image of the surface of a section of a ceramic brick containing 10 (a) and 50% (b) GCP sludge (brick firing temperature 1050°C): 1 – 7) sections chosen for microprobe analysis.

sults show that an increase of the exposure temperature results in a considerable increase of the concentration of the experimental ions in the extracts. Thus, as temperature increases from 20 to 50°C the migration of Ni²⁺ and Cr⁶⁺ increases 1.1 – 1.6-fold, Zn²⁺ and Cu²⁺ 1.19 – 1.45-fold, and total iron and Cr³⁺ 1.44 – 1.78 and 1.07 – 1.21-fold, respectively.

The concentrations of all experimental ions in ammonium-acetate extracts obtained by 30-day exposure at 50°C are presented in Table 1. Analysis of these data shows that the concentrations of the heavy-metal ions determined by photometry and atomic absorption spectroscopy (AAS) are quite close to within the unavoidable experimental error. As one can see in Table 1, when samples containing 50% sludge are kept in a model medium the MAC is exceeded by 0.12 – 0.14 mg/liter for total iron and 0.11 – 0.14 mg/liter and 0.013 – 0.015 mg/liter for tri- and hexavalent chromium, respectively. The Cr⁶⁺ concentration in extracts also exceeds the MAC by a small amount for samples containing 40% sludge.

In summary, under the most stringent model exposure conditions (30 days at 50°C in ammonium-acetate buffer solution) the experimental samples containing to 30% GCP sludge inclusively, completely satisfy GN 2.1.5.10-21-2003 [7] with respect to normalization of migration of all experimental chemical elements.

It is well known that the migration of chemical elements through ceramic samples depends directly on their structural features (the porosity, pore distribution, pore size and shape, state of the surface, degree of crystallization and ratio of the crystalline and glassy phases). To explain the regularities in the migration of the chemical elements the phase composition and structure of the materials were studied in detail with a D 8 Advance diffractometer (Bruker, Germany) and a JSM-560 LV electron microscope, equipped with an EDX JED-2201 JEOL (Japan) electron-probe energy-dispersive local chemical analysis system.

The ceramic brick samples obtained (Fig. 2) have a quite complex structure, represented by a combination of crystalline, glassy and gas phases with different quantitative ratios. A study of the chemical composition of local sections 1 – 7 of the ceramic samples (see Fig. 2, Table 2) established the

TABLE 2. Chemical Composition in Different Local Sections (see Fig. 2), Obtained by Electron-Probe Microanalysis

Local section	Oxide content, wt. %											
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	FeO+Fe ₂ O ₃	TiO ₂	Cr ₂ O ₃	CuO	ZnO	NiO
1	9.28	4.42	1.06	0.61	0.12	0.54	81.58	0.47	1.91	–	0.01	–
2	55.97	16.91	8.25	2.89	1.66	2.64	10.48	0.87	0.33	–	–	–
3	68.91	11.85	3.46	3.94	3.99	4.12	4.27	–	0.02	0.41	0.02	0.01
4	89.06	5.05	2.07	0.44	0.24	0.50	1.86	0.47	0.30	–	0.01	–
5	3.28	1.42	0.16	0.51	0.02	0.54	91.87	0.07	2.09	–	0.04	–
6	55.71	8.49	2.02	2.98	1.08	1.72	55.71	0.87	3.72	0.33	2.08	1.85
7	81.67	3.59	1.69	0.59	0.24	1.46	8.52	0.47	1.75	–	0.02	–

following regularities. The structural formations designated as local sections 1 and 7 are characterized by elevated total iron (II, III) and probably belong to iron-containing sections with some impurities of other oxides. The local section 2, characterized by elevated SiO₂, Al₂O₃ and CaO together with other oxides, belong to an aluminum silicate phase — anortite. The local section 3, comprising interlayers connecting structural elements, is characterized by, together with 68.91% SiO₂ and 11.85% Al₂O₃, elevated quantities of the oxides of alkali and alkali-earth elements (1.99% Na₂O, 4.12% K₂O and 3.94% MgO), which in our opinion can be identified as a glassy phase. The local sections 4 and 5 characterized by high SiO₂ content can be associated to a composition with α -quartz predominating while the presence in these sections of a small quantity of Al₂O₃ (5.05%) and RO+R₂O+R₂O₃ (5.12%) attests to an amorphized clayey component. The local section 6 characterized by elevated content of silicon, aluminum and iron oxides probably belongs to amorphized clayey matter saturated with iron oxides.

Analysis of the data in Table 2 shows that the Cu²⁺, Zn²⁺ and Ni²⁺ ions are predominately components of amorphized clayey matter (section 6) and a glassy phase (section 3). In addition, in the structure of the silicates the transition element cations are not components of silicon-oxygen radicals but rather they lie outside them, neutralizing the charge of nonbridge oxygen atoms in a silicon-oxygen radical and bonding these radicals with one another [8]. In this connection the ions present in the structure of the glassy phase are more mobile than the ions occupying interstices of the crystal lattice. In addition, it is noted in [9] that ion-exchange diffusion is present at the contact boundary of the glass phase and solutions of different nature. In addition, the H⁺ ions formed in a solution as a result of partial dissociation of distilled water can be observed to diffuse to vacant sites of the crystal lattice of mineral present in the material.

The Fe²⁺ and Fe³⁺ ions are present in the amorphized phases (sections 3 and 6) as well as structural formations (sections 1 and 7), which x-ray phase analysis identifies as hematite α -Fe₂O₃, maghemite γ -Fe₂O₃ and magnetite Fe₃O₄ (Fig. 3). It is known from the published data that the ions present in the crystalline phases exhibit low mobility since

movement along interstices is due to the presence of lattice defects and vacancies. For this reason, bi- and trivalent iron ions are characterized by low migration levels compared with their content in the GCP sludge and correspondingly in the samples obtained.

As one can see from Table 2, an elevated content of chromium ions is observed in sections belonging to iron-containing crystalline phases, which could indicate that these ions are present in the structure of maghemite. It is assumed that Cr³⁺ ions participate in the formation of γ -Fe₂O₃, filling in it a cationic vacancy and thereby increasing the stability of the metastable phase of maghemite right up to 1050°C, while a lower temperature of the polymorphic transition of γ -Fe₂O₃ into α -Fe₂O₃ is indicated in the literature — 550 – 650°C [8].

It should be noted that x-ray diffraction studies have not revealed crystalline phases containing copper, nickel, chromium and zinc ions. This is explained by the impossibility of identifying these phases because the amounts are negligible and the dispersity high and they are fixed in the x-ray amorphous phases. The presence of small quantities of chromium and zinc ions in sections belonging to quartz, anortite and iron-containing phases (see Table 2) could mean that they can be adsorbed on phase interfaces.

As indicated above, most ions (60 – 80%) are washed out of the ceramic sample on the first day of exposure. In this connection it can be assumed that migration proceeds predominately from the surface layers of the sample. Ion diffusion from the center to the surface of the material is limited by a dense and quite complicated structure of the sample as well as by the presence of closed pores and low porosity, which are due to the semidry pressing and sintering processes.

The published data and research suggest that the migration of the ions of heavy elements from a sample into distilled water is due to a complex of physical-chemical processes occurring at the interface of solid – liquid phases, among which ion diffusion, hydrolysis of salts of polysilicic acids and, to a very low degree, dissolution can be identified. The increase in the migration in acid media compared with distilled water is probably due to the more intense dissolution of the main crystalline phases. Silicates and alumino-si-

licates, in whose form ceramic material is represented, can also enter into a reaction with acetic acid and ammonium hydroxide present in the solution. Diffusion and chemical processes occurring simultaneously result in the formation of mixed complex compounds incorporating the ligands NH_3 , H_2O , OH^- and CH_3COO^- in which the heavy-metal ions enter as complex-forming agents. The relatively low migration of chromium ions in an acidic medium compared with the migration of all other elements studied are in good agreement with the well-known notion that chromium compounds are highly stable.

The increase in the migration of heavy metal ions with increasing temperature can probably be explained by intensification of physical-chemical processes and reduced viscosity of the model medium.

The maximum possible concentration of ions in extracts was calculated on the basis of data on the chemical compositions of the ceramic bodies. The degree of migration of the ions was calculated as the ratio of the actual migration to the maximum possible value (see Table 1). The minimum migration from the experimental samples is characteristic for iron and nickel ions (0.0003 – 0.006 and 0.0075 – 0.014%, respectively). In the opinion of the authors, the low migration of Fe^{2+} and Fe^{3+} is due to their strong fixation in the crystal structure of magnetite, maghemite and magnetite as well as the high energy of the Fe–O bond, equal to 410.5 kJ/mole [10]. The degree of migration of chromium and zinc ions is 0.01 – 0.033%. The maximum migration is observed for Cu^{2+} ions (0.329 – 0.640%); this is explained by the lower energy of the Cu – O bond, comprising 267 kJ/mole [10].

In summary, the following conclusions can be drawn from this work.

1. The migration of heavy metal ions from a sample of facing ceramic brick depends on a number of factors. Increases in the holding time from 1 to 30 days, decrease in pH from 7 to 4.5, the exposure temperature from 20 to 50°C and the sludge content and correspondingly the content of chemical elements in ceramic body result in higher, the greatest effect being due to the exposure time and pH of the medium.

2. In our opinion the migration of ions of heavy elements from samples into the model medium can be explained by a complicated complex of physical-chemical processes occurring simultaneously at solid – solution interfaces: ion diffusion, hydrolysis of salts of polysilicic acids and their interaction with ammonium hydroxide and acetic acid as well as weak dissolution stand out.

It was established that migration proceeds predominately from the surface layers of a sample and that the ions diffusion from the bulk is limited by the quite dense structure of the material, comprising a combination of glassy and crystalline phases as well as, the presence of closed pores. In addition, the migration of different chemical elements depends explicitly on the structural features and phase composition of the new materials as well as on the characteristics of the ion distribution in the structure.

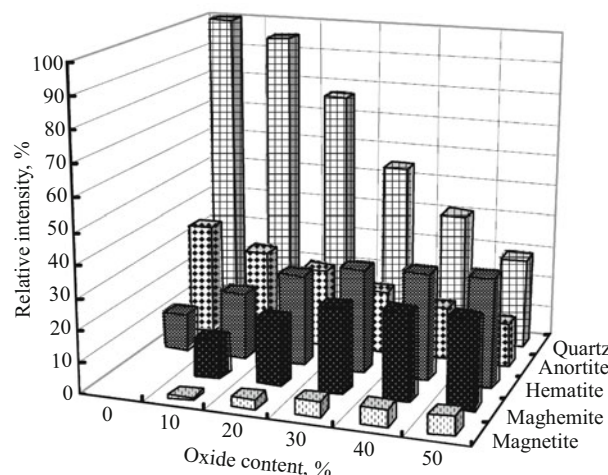


Fig. 3. Intensity of diffraction peaks of crystalline phases in samples of ceramic bricks versus the content of GCP sludge with firing temperature 1050°C.

3. It was determined that the migration of the ions studied under the most difficult operating conditions (30-day exposure at 50°C in an ammonium-acetate buffer solution) from brick samples containing to 30% sludge inclusively fully satisfy the requirements GN 2.1.5.10-21–2003 [7] for the content of chemical elements in the residential drinking and public water systems.

Since under real operating conditions for ceramic brick only one side of an article, and not the entire sample as in the case of the present studies, is exposed to the atmosphere, the migration is expected to be lower than the values presented. In this connection the use of up to 30% inclusively of iron-containing sludge in ceramic bodies makes it possible to obtain high-quality durable building materials with the required decorative and physical-technical characteristics as well as to solve the problems of resource conservation and recycling of industrial wastes without harming the environment or human health.

REFERENCES

1. É. A. Kucheroва, L. N. Tatski, and A. Yu. Panichev, "Some applications of electroplating sludge for obtaining ceramic materials and articles," in: *Efficient Use of Natural Resources and Protection of the Environment, Coll. Works* [in Russian], Lenin-grad (1987), Issue 10, pp. 24 – 36.
2. E. O. Bogdan and I. A. Levitskii, "On the possibility of using electroplating wastes in the production of architectural ceramic," *Stroit. Nauka Tekh.*, No. 3, 17 – 21 (2009).
3. I. S. Bitel', I. A. Levitskii, and N. I. Zayats, "Transparent vitreous coatings with low migration of boron and aluminum ions into acetic acid extracts," *Steklo Keram.*, No. 7, 20 – 24 (2006); I. S. Bitel', I. A. Levitskii, and N. I. Zayats, "Transparent vitreous coatings with decreased migration of boron and aluminum ions into acetic acid extracts," *Glass Ceram.*, **63**(7–8), 230 – 234 (2006).

4. D. L. Orlov, G. V. Kochetkova, K. S. Katkova, et al., "Assessment of the hygienic properties of glass containers," *Steklo Keram.*, No. 12, 23 (1981); D. L. Orlov, G. V. Kochetkova, K. S. Katkova, et al., "An evaluation of the health-safety properties of glass containers," *Glass Ceram.*, **38**(12), 648–649 (1981).
5. *Sanitary-Hygienic Assessment of Building Materials with the Addition of Industrial Wastes: Instructions, MU 2.1.674–97* [in Russian], Introduced August 8, 1997, RF State System of Sanitary Epidemiological Normalization, Moscow (1997).
6. Yu. Yu. Lur'e, *Analytical Chemistry of Industrial Waste Waters* [in Russian], Khimiya, Moscow (1984).
7. *Maximum Admissible Concentration (MAC) of Chemical Substances in Domestic and Residential Water Supply, GN 2.1.5.10-1-2003: Hygienic Norms for Communal Hygiene* [in Russian], Introduced January 1, 2002, Minsk (2002).
8. V. S. Gorshkov, V. G. Savel'ev, and N. F. Fedorov, *Physical Chemistry of Silicates and Other Refractory Compounds* [in Russian], Vyssh. Shkola, Moscow (1988).
9. A. Escardino, et al., "Leand release from bisilicate ceramic glaze in acid media. I. Process, mechanism and kinetics," *Trans. J. Brit. Ceram.*, **86**(2), 47–51 (1987).
10. V. A. Rabinovich and Z. Ya. Khavin, *Brief Handbook of Chemistry* [in Russian], Khimiya, Leningrad (1978).